

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
23 December 2004 (23.12.2004)

PCT

(10) International Publication Number
WO 2004/111170 A1

(51) International Patent Classification⁷: **C11D 3/386**,
1/12, 1/08 PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(21) International Application Number:

PCT/EP2004/050966

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:
VA2003A000019 13 June 2003 (13.06.2003) IT

Declaration under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AB, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

(54) Title: AQUEOUS LIQUID DETERGENT COMPOSITIONS COMPRISING ANIONIC ESTERS OF ALKYL POLYGLYCOSIDES AND ENZYMES

(57) Abstract: The present invention is related to aqueous liquid detergent compositions comprising anionic esters of alkylpolyglycosides and enzymes, and to the procedure for their preparation; the aqueous liquid detergent compositions of the invention exhibit long term enzymatic stability and excellent washing performance.

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Description**Aqueous liquid detergent compositions comprising anionic esters of alkylpolyglycosides and enzymes.****Technical field**

- [0001] This invention is related to aqueous liquid detergent compositions comprising anionic esters of alkylpolyglycosides and enzymes, and to the procedure for their preparation.
- [0002] The aqueous liquid detergent compositions of the invention exhibit long term enzymatic stability and excellent washing performance.

Background Art

- [0003] It is well known that washing performance of detergents is mainly due to their surfactant composition.
- [0004] In the majority of cases, such surfactant composition is made of mixtures of anionic, non-ionic, and, in some case, of amphoteric surfactants.
- [0005] The best washing performance is usually obtained by using a combination of anionic and non-ionic surfactants.
- [0006] In recent years, detergent compositions in powder form with improved washing performance by the presence of one or more enzymes have increased their market share.
- [0007] The preparation and use of powder detergent formulations comprising enzymes, in addition to the usual problems related to dusting, may lead to sensitisation in selected individuals if inhaled.
- [0008] On the other hand, the incorporation of one or more enzymes in aqueous liquid detergent compositions can represent considerable technical problems due to the fact that enzymes can be rapidly inactivated in an aqueous environment in the presence of anionic surfactants, which are a fundamental component of detergents.
- [0009] Such problems of compatibility between enzymes and surfactants occur to a less extent with non ionic surfactants, as their inactivation effect on enzymes is lower.
- [0010] The inactivation of enzymes in liquid aqueous detergent formulations has been investigated and described in the literature, for example in KRAVETZ, L., et al. Effect of surfactant structure on stability of enzymes formulated into laundry liquids. *Journal of the American Oil Chemists'*

society. 1985, vol.62, no.5, p.943-949. and in RUSSEL, Geoffry L., et al. Use of certain alcohol ethoxylates to maintain protease stability in the presence of anionic surfactants. *Journal of surfactants and detergents.* 2002, vol.5, no.1, p.5-10.

- [0011] In the known techniques the use of stabilisers or of mixtures of stabilisers is suggested in order to improve the stability of enzymes in aqueous liquid detergent compositions.
- [0012] As an example, we cite the stabilisers or mixtures of stabilisers described in US 4,305,837, US 4,318,818, US 4,537,707, US 4,670,179, US 4,949,179, US 5,071,586, US 5,156,773, US 6,121,225; however, these stabilisers only prevent or delay the inactivation of enzymes, without contributing in any way to the overall washing performance of the detergent mix.
- [0013] Another possibility is to improve the stability of enzymes in aqueous detergent compositions by modifying the surfactant compositions.
- [0014] This can be obtained, for example, by increasing the amount of non-ionic surfactants and at the same time by reducing the amount of anionic surfactant, as described in WO 9845396.
- [0015] It is nevertheless still highly desirable to provide anionic surfactants, which, when incorporated in aqueous liquid detergents, could exhibit little inactivating effect on enzymes, or at least surfactants which exhibit a inactivating effect smaller than the one of traditional anionic surfactants.
- [0016] It is further desirable to provide anionic surfactants that, when incorporated in aqueous liquid detergents, can contribute to the washing performance of said mixtures at least as much as the traditional anionic surfactants.

Disclosure of Invention

- [0017] It has now surprisingly been found that, in aqueous liquid detergent compositions, anionic esters of alkylpolyglycosides exhibit a low inactivating effect on enzymes, in comparison with the normally used anionic surfactants.
- [0018] The anionic esters of alkylpolyglycosides, which are described for example in EP 510,564 and in EP 510,565, show in aqueous liquid detergent compositions, comprising them together with an enzyme, a better stability and washing performance than the traditional anionic surfactants.

[0019] It is therefore an object of the present invention an aqueous liquid detergent composition showing high enzymatic stability and washing performance and comprising:

[0020] a. from 0.1 to 70% by weight (wt%), preferably from 10 to 30 wt%, of one or more anionic surfactant selected among anionic ester of alkylpolyglycosides having general formula:

[0021] $[R-O-(G)_x]_n-(D)_y \quad (I)$

[0022] wherein:

[0023] R is an aliphatic group, saturated or unsaturated, linear or branched, having from 6 to 20 atoms of carbon, preferably from 8 to 16 atoms of carbon;
G is a residue of a reducing saccharide, preferably of glucose, connected to R-O by means of an ethereal O-glycosidic bond;

[0024] O is an oxygen atom;
D is an acyl residue of sulfosuccinic acid or of a carboxylic acid selected from the group consisting of citric, tartaric, maleic and malic acid, connected to an oxygen atom of G;
n is a number between 1 and m-1, where m is the number of carboxylic groups in the acid that originates D;
x is a number from 1 to 10, representing the average degree of oligomerization of G;
y is a number from 1 to 10 representing the degree of average esterification of $(G)_x$.

[0025] b. from 0.05 to 10 wt%, preferably from 0.10 to 5 wt%, of an enzyme selected in the group consisting of proteases, amylases, lipases, cellulases and mixture thereof;

[0026] c. from 10 to 95 wt%, preferably from 20 to 70 wt%, of water.

[0027] The preferred anionic esters of alkylpolyglycosides useful for the realisation of the present invention are: alkylpolyglucoside citrate disodium salt, alkylpolyglucoside sulfosuccinate disodium salt and alkylpolyglucoside tartrate sodium salt, which are respectively available on the market under the trade names Eucarol ® AGE EC, Eucarol ® AGE SS, Eucarol ® AGE ET (Cesalpinia Chemicals, Italy).

- [0028] In addition to the above described essential constituents, the aqueous liquid detergent compositions of the invention may contain from 0.1 to 50 wt%, preferably from 10 to 30 wt%, of one or more anionic surfactants having general formula different from (I), in amount not exceeding the amount of the surfactants having general formula (I).
- [0029] In particular, the anionic surfactants having general formula different from (I) are chosen among linear or branched C₈-C₁₅ alkylsulfate, linear or branched C₈-C₁₅ alkylbenzenesulfonates; C₈-C₂₄ polyethoxylated alkyl ether sulfates containing from 1 to 20 ethoxylic groups.
- [0030] The aqueous liquid detergent compositions of the invention may further contain non-ionic surfactants, such as: C₈-C₁₈ ethoxylated and/or propoxylated fatty alcohols containing from 1 to 20 ethoxyl or propoxyl groups and C₈-C₁₈ ethoxylated and/or propoxylated alkylphenols containing from 1 to 20 ethoxyl or propoxyl groups.
- [0031] The aqueous liquid detergent compositions of the invention may further contain cationic and amphoteric surfactants.
- [0032] It is a further fundamental object of the present invention a procedure for the preparation of aqueous liquid detergent compositions having high enzymatic stability comprising the following steps (wt% are referred to the final composition):
- [0033] A. from 0.1 to 70 wt%, preferably from 10 to 30 wt%, of one or more anionic surfactants selected among anionic ester of alkylpolyglycosides having general formula:
- [0034] [R-O-(G)_x]_n-(D)_y (I)
- [0035] wherein:
- [0036] R is an aliphatic group, saturated or unsaturated, linear or branched, having from 6 to 20 atoms of carbon, preferably from 8 to 16 atoms of carbon;
G is a residue of a reducing saccharide, preferably of glucose, connected to R-O by means of an ethereal O-glycosidic bond;
- [0037] O is an oxygen atom;
D is an acyl residue of sulfosuccinic acid or of a carboxylic acid selected from the group consisting of citric, tartaric, maleic and malic acid, connected to an oxygen atom of G;

n is a number between 1 and m-1, where m is the number of carboxylic groups in the acid that originates D;

x is a number from 1 to 10, representing the average degree of oligomerization of G;

y is a number from 1 to 10 representing the degree of average esterification of (G)_x.

- [0038] are mixed with from 10 to 95 wt%, preferably from 20 to 70 wt%, of water, under stirring;
- [0039] B. the mixture is stirred for 10-30 minutes at a temperature of 15-30°C, and the pH is adjusted to 4-8;
- [0040] C. from 0.05 to 10 wt% of an enzyme selected in the group consisting of proteases, amylases, lipases, cellulases and mixture thereof is added while stirring.
- [0041] According to a preferred aspect of the invention, after step A., from 0.1 to 50 wt%, preferably from 10 to 30 wt%, of one or more anionic surfactants having general formula different from (I) are added while stirring to the obtained mixture, said anionic surfactants being added in an amount not exceeding the amount of the surfactant having general formula (I); preferably the anionic surfactants having general formula different from (I) are chosen among linear or branched C₉-C₁₅ alkylsulfate, linear or branched C₉-C₁₅ alkylbenzenesulfonates, C₈-C₂₄ polyethoxylated alkyl ether sulfates containing from 1 to 20 ethoxylic groups.
- [0042] The enzymes useful for the realisation of the invention are the enzymes commercially available and normally used in detergent compositions.
- [0043] Among those, proteases are the preferred ones, and alkaline proteases are the most preferred ones.
- [0044] As commercial sources of enzymatic preparations comprising alkaline proteases, we cite by way of example, but not to be limited, the products sold by Genencor under the trade name Puraject® and the products sold by Novozymes under the trade name Savinase®, Durazyme® and Esperase®.
- [0045] Other additives which are normally present in aqueous liquid detergents may be contained in the aqueous liquid detergent compositions of the invention; by way of example we cite: optical brighteners, softeners, anti-

foams, foaming agents, perfumes, dyes, stabilisers, suspending agents, biocides, pH regulators, sequestering agents.

- [0046] The aqueous liquid detergent compositions of the invention may be used in household cleaning (on various surfaces, stoves, floors, glasses, sanitary wares) and for the washing of laundry, but they can also be used as heavy duty cleaning liquid detergents (HDLD).
- [0047] The following examples illustrate the improved enzymatic stability and the good washing performance of the aqueous liquid detergent compositions of the invention; they are not intended to unduly limit the Invention itself.
- [0048] In the examples the following anionic esters of alkylpolyglycosides have been used, all sold by Cesalpinia Chemicals SpA:
- [0049] Eucarol ® AGE EC = alkylpolyglucoside citrate disodium salt, 30 wt% active substance (a.s.);
- [0050] Eucarol ® AGE ET = alkylpolyglucoside tartrate sodium salt, 30 wt% a.s.;
- [0051] Eucarol ® AGE SS = alkylpolyglucoside sulfosuccinate disodium salt, 45% a.s.;
- [0052] The following traditional anionic surfactants have also been used, all commercialised by Cesalpinia Chemicals SpA:
- [0053] Chimpon BAC = sodium dodecylbenzenesulfonate, 50 wt% a.s.;
- [0054] Rolpon 24/230 = sodium laurylether(2)sulfate, 27 wt% a.s.;
- [0055] Rolpon LS = sodium laurylsulfate, 28 wt% a.s..
- [0056] The following methods of evaluation of the washing performance and of the residual protease activity were used:
- [0057] Determination of the average percentage of stain removed.
- [0058] The washing performance (average percentage of stain removed) is determined on polyester/cotton 65/35, using commercial ketchup as standard stain.
- [0059] About 3 ± 0.001 g of ketchup are deposited on a fabric swatch and sandwiched between a second swatch, over which a 500 ± 0.01 g weight is applied for 15 minutes. The stained swatches are left drying overnight at 20°C and 65% humidity in a conditioned room.
- [0060] The swatches are then washed in Linitest Plus (Atlas) at 40°C for 30 min., each test at 1 g/l active substance with water at 25°F hardness.
- [0061] After washing, the swatches are air dried for 15 hours.

- [0062] Reflectance is evaluated on the Datacolor spectrometer according to the Berger method with a D65/10 light source.
- [0063] The percentage of stain removed is calculated by the equation:
- [0064]
$$\% \text{ of stain removed} = [(A-B)/(C-B)] \times 100$$
- [0065] where A is the reflectance after washing, B the reflectance before washing and C the reference reflectance value of the unstained, white swatch (measured before starting each trial).
- [0066] The average percentage of stain removed is calculated as the average value from three tests.
- [0067] Evaluation of the protease activity
- [0068] The evaluation of the protease activity (PA) is based on the following principle: the protease hydrolyses azocasein in 20 minutes at 40°C, when the protease is dosed at 1 wt% in an aqueous mixture at pH 8 (0.1M Tris/HCl, 1.25mM CaCl₂).
- [0069] The portion of azocasein which has not been hydrolysed is precipitated with trichloroacetic acid, while the hydrolysed azocasein is determined by spectrophotometry in the visible light spectrum.
- [0070] The protease activity is defined as mg of azocasein hydrolysed per minute and gram of enzymatic preparation.
- [0071] The initial protease activity (PA_i) is the protease activity measured immediately after the preparation of the composition containing the protease.
- [0072] The percentage residual protease activity (%RPA) is
- [0073]
$$\%RPA = (AP_t/AP_i) \times 100$$
- [0074] where AP_t is the protease activity of the composition at the time %RPA is measured.
- [0075] Example 1.
- [0076] Test of enzymatic stability of aqueous detergent compositions of the invention.
- [0077] Aqueous based liquid detergent compositions are prepared which contain 0.1 wt% of Purafect ® 4000 L (alkaline protease from B subtilis OGM by Gennecor, US) and variable amounts of anionic ester of alkylpolyglycosides (see the first column of Table 1)

[0078] Similar compositions (comparative) having the same percentage of Purafect ® 4000 L and with variable amounts of traditional anionic surfactants (see the first column of Table 1) are prepared.

[0079] The enzymatic stability of the compositions is evaluated by measuring the %RPA one hour after their preparation, using the method above described; from the time of their preparation to the time when the PA_t is measured the compositions are maintained at 30°C.

[0080] The %RPA is reported in Table 1.

[0081]

Table 1

% a.s.*	%RPA					
	Eucarol AGE EC	Eucarol AGE ET	Eucarol AGE SS	Chimpon BAC**	Rolpon 24/230**	Rolpon LS**
0.01	100	100	100	85	89	-
0.05	100	100	100	26	87	-
1	100	100	100	19	85	0
5	100	100	100	15	65	-
10	100	100	100	0	-	-

[0082] *wt% of active substance of the surfactant in the composition

[0083] **comparative compositions

[0084]

[0085] Example 2.

[0086] Test of enzymatic stability of aqueous detergent compositions of the invention.

[0087] Aqueous based detergent compositions are prepared containing 0.15 %v of Savinase ® 16L (alkaline protease from *B. subtilis* OGM by Novozymes, DK) and variable amounts of anionic ester of alkylpolyglycosides (see the first column of Table 2)

[0088] Similar compositions (comparative) having the same percentage of Savinase ® 16L and with variable amounts of traditional anionic surfactants (see the first column of Table 2) are prepared.

[0089] The enzymatic stability of the compositions is evaluated by measuring the %RPA one hour after their preparation, using the method above

described; from the time of their preparation to the time when the PA_t is measured the compositions are maintained at 30°C.

[0090] The %RPA is reported in Table 2.

[0091]

Table 2

% a.s.*	%RPA					
	Eucarol AGE EC	Eucarol AGE ET	Eucarol AGE SS	Chimpon BAC**	Rolpon 24/230**	Rolpon LS**
0	100	100	100	100	100	-
1	100	100	100	29	68	-
5	100	100	100	26	52	0
10	100	100	100	25	-	-

[0092] *wt% of active substance of the surfactant in the composition

[0093] **comparative compositions

[0094]

[0095] Example 3:

[0096] Test of enzymatic stability of aqueous detergent compositions of the invention.

[0097] Aqueous based detergent compositions are prepared containing 0.4 %v of Purafect ® OX 4000L (alkaline protease from B subtilis OGM by Genencor, US) and variable amounts of anionic ester of alkylpolyglycosides (see the first column of Table 3)

[0098] Similar compositions (comparative) having the same percentage of Purafect ® OX 4000L and with variable amounts of traditional anionic surfactants (see the first column of Table 3) are prepared.

[0099] The enzymatic stability of the compositions is evaluated by measuring the %RPA one hour after their preparation, using the method above described; from the time of their preparation to the time when the PA_t is measured the compositions are maintained at 30°C.

[0100]

[0101]

[0102] The %RPA is reported in Table 3.

[0103]

Table 3

% a.s.*	%RPA					
	Eucarol AGE EC	Eucarol AGE ET	Eucarol AGE SS	Chimpon BAC**	Rolpon 24/230**	Rolpon LS**
0	100	100	100	100	100	-
1	100	100	100	19	77	-
5	100	100	100	0	60	0
10	100	100	100	0	54	-

[00104] *wt% of active substance of the surfactant in the composition

[00105] **comparative compositions

[00106]

[00107] Example 4.

[00108] Test of washing performance and enzymatic stability of aqueous detergent compositions of the invention.

[00109] Aqueous detergent compositions from 1 to 17 are prepared as follows.

[00110] 25 g of surfactant(s) (see Table 4, where the amount of a.s. of surfactant in grams in each composition is reported) are diluted with 69.5 g of demineralised water, under stirring.

[00111] In sequence, under stirring, 0.5 g of protease (Purafect ® 4000 L) and 5 g of monopropylene glycol are added.

[00112] The mixture is stirred for 15 minutes and the pH is regulated at 7.4-7.6 with citric acid or triethanolamine.

[00113] The washing performance is determined by measuring the average percentage of stain removed, using the above described method.

[00114] The average percentage of stain removed (%SR) is reported in Table 4 for each composition.

[00115] The enzymatic stability of Compositions 1-17 is evaluated by measuring the %RPA one hour after their preparation, using the method above described; from the time of their preparation to the time when the PA_t is measured the compositions are maintained at 40°C.

[00116]

[00117] The %RPA of Compositions 1-17 are reported in Table 4.

[00118]

Table 4

Comp.	1	2	3	4	5	% SR	%APR
1*				25		56.0	0
2*					25	54.5	74
3*			25			55.8	29
4	25					60.8	100
5		25				77.6	100
6*	5			20		54.0	-
7	10			10		55.0	36
8	20			5		56.0	-
9*	5				20	60.1	-
10	10				10	59.0	79
11	20				5	59.8	-
12*		5		20		56.1	0
13		10		10		65.2	56
14		20		5		75.6	65
15*		5			20	62.6	-
16		10			10	65.9	85
17		20			5	70.6	100

[00119] * comparative compositions

[00120] 1 = Eucarol ® AGE EC

[00121] 2 = Eucarol ® AGE SS

[00122] 3 = Rolpon LS

[00123] 4 = Chimpon BAC

[00124] 5 = Rolpon 24/230

Claims

1. Aqueous liquid detergent composition comprising:
 - a. from 0.1 to 70% by weight (wt%) of one or more anionic surfactant selected among anionic ester of alkylpolyglycosides having general formula:
$$[R-O-(G)_x]_n-(D)_y \quad (I)$$
wherein:

R is an aliphatic group, saturated or unsaturated, linear or branched, having from 6 to 20 atoms of carbon, preferably from 8 to 16 atoms of carbon;

G is a residue of a reducing saccharide, preferably of glucose, connected to R-O by means of an ethereal O-glycosidic bond;

O is an oxygen atom;

D is an acyl residue of sulfosuccinic acid or of a carboxylic acid selected from the group consisting of citric, tartaric, maleic and malic acid, connected to an oxygen atom of G;

n is a number between 1 and m-1, where m is the number of carboxylic groups in the acid that originates D;

x is a number from 1 to 10, representing the average degree of oligomerization of G;

y is a number from 1 to 10 representing the degree of average esterification of (G)_x;
 - b. from 0.05 to 10 wt% of an enzyme selected in the group consisting of proteases, amylases, lipases, cellulases and mixture thereof;
 - c. from 10 to 95 wt% of water.
2. Aqueous liquid detergent composition according to claim 1., comprising from 10 to 30 wt% of anionic surfactant having general formula (I).
3. Aqueous liquid detergent composition according to claim 1., comprising from 0.10 to 5 wt% of one or more enzymes of point b.
4. Aqueous liquid detergent composition according to claim 1., comprising from 20 to 70 wt% of water.
5. Aqueous liquid detergent composition according to any of the preceding claims, further comprising from 0.1 to 50 %wt of one or more anionic surfactants having general formula different from (I), in amount not exceeding the amount of the surfactants having general formula (I).

6. Aqueous liquid detergent composition according to claim 5., comprising from 10 to 30 %wt of one or more anionic surfactants having general formula different from (I).
7. Aqueous liquid detergent composition according to claim 6., where the anionic surfactants having general formula different from (I) are chosen among linear or branched C₈-C₁₅ alkylsulfate, linear or branched C₈-C₁₅ alkylbenzenesulfonates, C₈-C₂₄ polyethoxylated alkyl ether sulfates containing from 1 to 20 ethoxylic groups.
8. Procedure for the preparation of aqueous liquid detergent compositions comprising the following steps, (wt% are referred to the final composition):
 - A. from 0.1 to 70 wt%, preferably from 10 to 30 wt%, of one or more anionic surfactants selected among anionic ester of alkylpolyglycosides having general formula:
$$[R-O-(G)_x]_n-(D)_y \quad (I)$$
wherein:
R is an aliphatic group, saturated or unsaturated, linear or branched, having from 6 to 20 atoms of carbon, preferably from 8 to 16 atoms of carbon;
G is a residue of a reducing saccharide, preferably of glucose, connected to R-O by means of an ethereal O-glycosidic bond;
O is an oxygen atom;
D is an acyl residue of sulfosuccinic acid or of a carboxylic acid selected from the group consisting of citric, tartaric, maleic and malic acid, connected to an oxygen atom of G;
n is a number between 1 and m-1, where m is the number of carboxylic groups in the acid that originates D;
x is a number from 1 to 10, representing the average degree of oligomerization of G;
y is a number from 1 to 10 representing the degree of average esterification of (G)_x
are mixed with from 10 to 95 wt%, preferably from 20 to 70 wt%, of water, under stirring;
 - B. the mixture is stirred for 10-30 minutes at a temperature of 15-30°C, and the pH is adjusted to 4-8;
 - C. from 0.05 to 10 wt% of an enzyme selected in the group consisting of

proteases, amylases, lipases, cellulases and mixture thereof is added while stirring.

9. Procedure for the preparation of aqueous liquid detergent compositions according to claim 8., wherein in step A. from 10 to 30 wt% of a mixture of anionic surfactant having general formula (I) are mixed with from 10 to 95 wt% of water.
10. Procedure for the preparation of aqueous liquid detergent compositions according to claim 8., wherein in step C. from 0.1 to 5 wt% of an enzyme selected in the group consisting of proteases, amylases, lipases, cellulases and mixture thereof is added while stirring.
11. Procedure for the preparation of aqueous liquid detergent compositions according to any of claims from 8. to 10., wherein after step A. from 0.1 to 50 wt% of one or more anionic surfactants having general formula different from (I) are added while stirring to the obtained mixture, said anionic surfactants being added in an amount not exceeding the amount of the surfactant having general formula (I).
12. Procedure for the preparation of aqueous liquid detergent compositions according to claim 11., wherein from 10 to 30 wt% of the anionic surfactants having general formula different from (I) are added.
13. Procedure for the preparation of aqueous liquid detergent compositions according to claim 12., wherein the anionic surfactants having general formula different from (I) are chosen among linear or branched C₈-C₁₅ alkylsulfate, linear or branched C₈-C₁₅ alkylbenzenesulfonates, C₈-C₂₄ polyethoxylated alkyl ether sulfates containing from 1 to 20 ethoxylic groups.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050966

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C11D3/386 C11D1/12 C11D1/08		
<p>According to International Patent Classification (IPC) or to both national classification and IPC</p>		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 86/05187 A (STALEY MFG CO A E) 12 September 1986 (1986-09-12) page 2, line 22 - line 27; claims 1-16 -----	1-13
A	US 6 121 225 A (BRITTON LARRY N ET AL) 19 September 2000 (2000-09-19) cited in the application claim 1 -----	1-13
A	EP 0 554 943 A (UNILEVER PLC ; UNILEVER NV (NL)) 11 August 1993 (1993-08-11) claims 1,2 ----- -/-	1-13
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents : °A° document defining the general state of the art which is not considered to be of particular relevance °E° earlier document but published on or after the international filing date °L° document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) °O° document referring to an oral disclosure, use, exhibition or other means °P° document published prior to the international filing date but later than the priority date claimed		
°T° later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention °X° document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone °Y° document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. °&° document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
3 November 2004		18/11/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016		Authorized officer Grittern, A

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	VERZOTTI T ET AL: "ESTERICI ALCHILOGLUCOSIDI (EUCAROL APG ESTERI). PER REALIZZARE DETERGENTI COSMETICI NATURALI, FUNZIONALI, DELICATI ED ECOLOGICI" COSMETIC NEWS, MILAN, IT, vol. 108, 5 June 1996 (1996-06-05), pages 183-186, XP000939060 ISSN: 1125-6222 the whole document	1

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